REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE:	3. REPORT TYPE AND DATES COVERED Final Report 1-Jul-2002 - 31-Dec-2005

4. TITLE AND SUBTITLE

Glass Formability and Diffusion Mechanisms in Bulk Metallic Glasses and Supercooled liquids

5. FUNDING NUMBERS

DAAD190210225

6. AUTHORS

Yue Wu

8. PERFORMING ORGANIZATION REPORT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES

University of North Carolina - Chapel Hill
Office of Sponsored Research
104 Airport Drive, Suite 2200, CB 1350
Chapel Hill, NC 27599 -1350

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

43717-MS.2

11. SUPPLEMENTARY NOTES

The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

12. DISTRIBUTION AVAILIBILITY STATEMENT

Approved for Public Release; Distribution Unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The abstract is below since many authors do not follow the 200 word limit

14. SUBJECT TERMS

bulk metallic glasses, supercooled liquids, glass transition, glass forming ability, NMR

15. NUMBER OF PAGES

Unknown due to possible attachments

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION ON THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev .2-89)
Prescribed by ANSI Std.
239-18 298-102

Report Title

Glass Formability and Diffusion Mechanisms in Bulk Metallic Glasses and Supercooled liquids

ABSTRACT

Three properties of bulk metallic glasses were investigated: (1) atomic motions; (2) characteristics of bonding and electronic states; (3) fracture. Atomic motion in glassy PdNiCuP was investigated by NMR over a wide temperature range from below the glass transition temperature Tg to above the liquidus temperature Tliq. This study reveals the temperature in the supercooled liquid region below which motions of different elements begin to diverge. It sheds light on the nature of the crossover temperature Tc proposed by mode coupling theory. Also, hopping was shown to persist below Tg. The electronic states of various metallic glasses were studied by NMR including CuZrAl, Ce-based, and Y-based alloys. Results established some correlation between the glass forming ability and the characteristics of electronic states. This sheds light on the structure and formation of metallic glasses. Finally, we studied the fracture surfaces of various bulk metallic glasses including the brittle Mg-based bulk metallic glass. We established a clear correlation between the fracture toughness and plastic process zone size for various glasses. The results indicate that the fracture in brittle metallic glassy materials might also proceed through the local softening mechanism but at different length scales.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Devitrification of Bulk Metallic Glass Zr41.2Ti13.8Cu12.5Ni10.0Be22.5 Studied by XRD, SANS, and NMR
X.-P. Tang, J. F. Löffler, W. L. Johnson, and Y. Wu
Journal of Non-Crystalline Solids 317, 118-122 (2003).

Magnetic Alignment in Nominally Non-Magnetic Hexagonal Metal Hydrides: NMR
Vikram D. Kodibagkar, Caleb D. Browning, Xiaoping Tang, Yue Wu, Robert C. Bowman, Jr. and Mark S. Conradi
Solid State NMR 24, 254–262 (2003).

Crossover of Microscopic Dynamics in Metallic Supercooled Liquid Studied by NMR
Lilong Li, Jan Schroers, and Yue Wu
Physical Review Letters 91, 265502 (2003).

Structural influence on atomic hopping and electronic states of Pd-based bulk metallic glasses
X.-P. Tang, Jörg F. Löffler, Ricardo B. Schwarz, William L. Johnson, Yue Wu
Applied Physics Letters 86, 072104 (2005).

Fracture of brittle metallic glasses: brittleness or plasticity
X. K. Xi, D. Q. Zhao, M. X. Pan, W. H. Wang, Y. Wu, J. J. Lewandowski
Physical Review Letters 94, 125510 (2005).

Number of Papers published in peer-reviewed journals: 5.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Quasicrystalline Compounds; Metallic Glasses
X.-P. Tang and Yue Wu
Encyclopedia of Nuclear Magnetic Resonance Volume 9, Advances in NMR (eds. D. M. Grant and R. K. Harris, John Wiley&Sons, Chichester, 2002). ISBN: 0-471-49082-2. p729-736.

Number of Papers published in non peer-reviewed journals: 1.00

(c) Papers presented at meetings, but not published in conference proceedings (N/A for none)

Number of Papers not Published: 0.00

(d) Manuscripts

Number of Manuscripts: 0.00

Number of Inventions:

Graduate Students

NAME	PERCENT_SUPPORTED	
Lilong Li	1.00	No
FTE Equivalent:	**1.00**	
Total Number:	**1**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED	
Alfred Kleinhammes	0.10	No
Xuekui Xi	0.10	No
FTE Equivalent:	**0.20**	
Total Number:	**2**	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Yue Wu	0.10	No
FTE Equivalent:	**0.10**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME	
Lilong Li	No
Total Number:	**1**

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Although significant progress has been made in the study of bulk metallic glasses (BMG), our understanding remains limited on the glass forming ability (GFA) and mechanical properties based on microscopic structures, chemical bonding, and dynamics. There are many difficulties in studying microscopic properties of BMGs because of the inaccessibility of the metallic state by many conventional techniques such as optical and dielectric measurements widely used in studying other types of glassy materials such as polymers. In this study, we showed that nuclear magnetic resonance (NMR) is a very useful technique that is able to probe various microscopic properties of metallic glasses and supercooled liquids including atomic motions, local structures, and characteristics of chemical bonding. In addition to the understanding of GFA and mechanical properties, such study also sheds light on the fundamental question of the nature of glass transition.

Statement of the problem studied

Here are some of the specific issues we have addressed. (1) The rate of thermal fluctuations on microscopic scale and its temperature dependence determine the properties of liquid/supercooled liquid and the corresponding glass transition. Macroscopic properties are related to the behavior of microscopic thermal fluctuations. For instance, the viscosity η and the relaxation time τ of microscopic thermal fluctuation are related to each other as described by the mechanical Maxwell equation, $\eta = G_\infty \tau$, where G_∞ is the high-frequency shear modulus. Among various theories, mode-coupling theory (MCT) predicts a qualitative change in the microscopic dynamics in the supercooled liquid at a crossover temperature T_c significantly above the glass transition temperature T_g. One of our focuses is to detect T_c and characterize the microscopic thermal fluctuations and dynamics in metallic supercooled liquids. (2) We investigated the characteristics of crystallization processes in some metallic glasses. Again, we demonstrated that NMR is very sensitive in detecting local structural changes and crystallization including in Al-based metallic glasses. Such investigations shed light on the crystallization mechanisms of metallic glasses and the GFA of metallic alloys. (3) We investigated the characteristics of the electronic states of various metallic glasses by NMR. Some common features of electronic states were identified in a series of BMGs including CuZrAl, Zr-based, and Y-based BMGs. Such common features could be directly linked to the superb GFA of these BMGs. (4) We studied the fracture surfaces of various bulk metallic glasses including the brittle Mg-based bulk metallic glass. We established a clear correlation between the fracture toughness and plastic process zone size for various glasses. The results indicate that the fracture in brittle metallic glassy materials might also proceed through the local softening mechanism but at different length scales.

Summary of the most important results

1. Detection of Atomic Fluctuation and Relaxation in Metallic Supercooled Liquids

Fast β relaxation In a liquid of densely packed atoms, an atom is temporarily trapped inside the cage formed by neighboring atoms and undergoes vibrations and rattling before escaping the cage. Here, the time dependence of the position vector $\vec{r}_i(t)$ of a given atom *i* can be described by $\vec{r}_i(t) = \vec{R}_i(t) + \vec{u}_i(t)$ where the rapidly changing $\vec{u}_i(t)$ describes local motions and the slowly varying $\vec{R}_i(t)$ describes the transition of the atom from one cage to another. A key distinction between the motions associated $\vec{R}_i(t)$ and $\vec{u}_i(t)$ is the temperature dependence of the characteristic times. While $\vec{R}_i(t)$ slows down rapidly upon cooling, the rate of $\vec{u}_i(t)$ does not

change much with temperature but its amplitude changes rapidly around T_c according to MCT. We have designed NMR experiments to measure both aspects of atomic motions.

MCT predicts that $\phi(q,t)$, the correlation function of density fluctuations with wave number q, undergoes a two-step relaxation process, called fast β-relaxation and α-relaxation. An important prediction of MCT is the temperature (T) dependence of $\vec{u}_i$ associated with the fast β-relaxation (possibly rattling). MCT predicts that

$$< u^2 >= u_c^2\left(1-\frac{1}{2}a\sqrt{(T_c-T)/T_c}\right)^2 \qquad (1)$$

below T_c where a>0 and u_c is the magnitude of rattling above T_c. Experimentally, the separation between the timescales of α and fast β relaxations in the temperature range of interest is often insufficient for model-independent determination of $\vec{u}_i$ by neutron scattering. So far, measurements of the effects of $\vec{u}_i$ have not revealed the critical behavior of $\vec{u}_i$ in metallic supercooled liquids. We designed an NMR approach to measure $\vec{u}_i$ since we proved that the average Knight shift is proportional to $< u^2 >$. Therefore, the temperature dependence of the Knight shift could reveal the critical behavior of dynamics predicted by MCT. Furthermore, NMR can also be used to measure the effect of $\vec{R}_i(t)$ (diffusion) such as the temperature dependence of the linewidth. These measurements confirm that there is indeed a critical behavior in dynamics in the supercooled liquid region. Figure 1 shows the temperature dependence of the ^{31}P Knight shift and the linewidth in PdNiCuP. The T-dependence of the shift below 580 K (T_g) is linear suggesting that $< \vec{u}^2 > \propto k_B T$ in the glassy state, as expected from equipartition theorem for harmonic vibrations. It is expected that K will depend more sensitively on T above T_g in the supercooled liquid region since sound velocities and elastic moduli in metallic glasses decrease above T_g. The observed linear T-dependence of K with a larger slope above 700 K indeed agrees

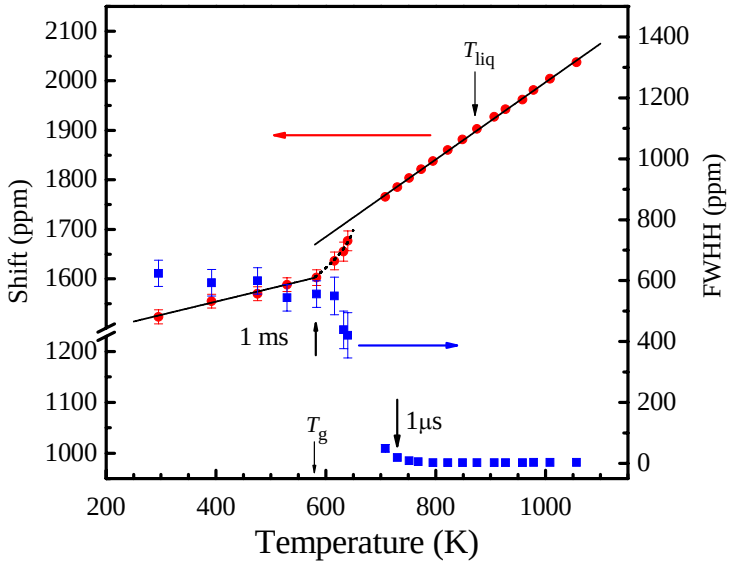

Figure 1. The average shift K measured versus T in the liquid, supercooled liquid, and glassy states (circle) as well as that of the crystallized sample (triangle). The T-dependence of the ^{31}P spectral linewidth (full width at half height) is also shown (square).

with this expectation. However, this could not explain the observed large positive offset of K from T_g to the extrapolated value based on the data above 700 K (see Fig. 1). We showed that this offset indicates that some $\vec{u}_i(t)$-associated atomic motion present in the liquid-like region decreases rapidly upon cooling below 700 K. A candidate of such atomic motion is the fast β-process associated with cage rattling. Since NMR is a local probe, it is particularly sensitive to such atomic motion. A fit of K is shown in Fig. 1 using with $T_c = 660 \pm 10$ K assuming the shift is proportional to $< u^2 >$ over the entire temperature range. This by no means implies that the change is abrupt at 660 K. The change might be gradual below 700 K and the effective T_c might be as high as 700 K. The detail is obscured by the lack of K data in that temperature range due to fast crystallization. This is a direct demonstration of the existence of the crossover process in metallic supercooled liquids.

The α-relaxation The observed temperature dependence of the ^{31}P linewidth provides a measure of the timescale of α relaxation related to the motion of $\vec{R}_i(t)$ in $\vec{r}_i(t) = \vec{R}_i(t) + \vec{u}_i(t)$. Since the static linewidth is of the order of 100 kHz, atomic diffusion on the timescale of 1 μs is needed to substantially reduce the line broadening. Simulations were done to extract the exact rate of motion associated with $\vec{R}_i(t)$ versus temperature. This technique, however, is not sensitive for probing rate of motions much faster than a few MHz as expected in the liquid and supercooled liquid states near the melting point. For this purpose, we used ^{63}Cu and ^{65}Cu NMR to study the rate of α-relaxation from above the liquidus temperature down to 800 K and below. We showed that the ^{65}Cu NMR linewidth in liquid PdNiCuP is determined by the spin-lattice relaxation rate induced by thermal fluctuations of the electric-field-gradient (EFG). It is known that

$$\Delta\nu = \frac{3(2I+3)}{2\pi I^2(2I-1)}\left(\frac{eQ}{\hbar}\right)^2 \int < V_{zz}(0) \bullet V_{zz}(t) > dt = \frac{3(2I+3)}{2\pi I^2(2I-1)} < \left(\frac{eQ}{\hbar}\left|V_0^{(2)}\right|\right)^2 > \tau_c \qquad (2)$$

where $< \left|V_0^{(2)}\right|^2 >$ is the thermally average-squared EFG and I is the spin number which is 3/2 for ^{65}Cu. τ_c is the correlation time of the EFG. The correlation of EFG decays if the Cu atom moves to a different cage (illustrated in Fig. 2) or if the shape or orientation of the cage changes significantly, for instance, by having a new nearest neighbor to the Cu atom or by distortion. In all these scenarios, the correlation time τ_c describes the time during which the cage around Cu remains rigid (other than vibrations). The time τ_c is clearly related to the α-relaxation and viscosity since the change of cage shape and orientation is required for viscous flow.

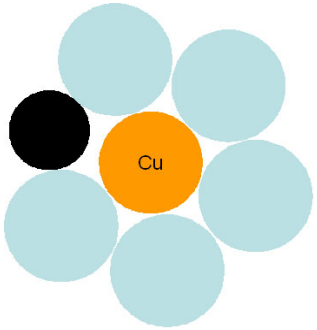

Figure 2. An illustration of the cage.

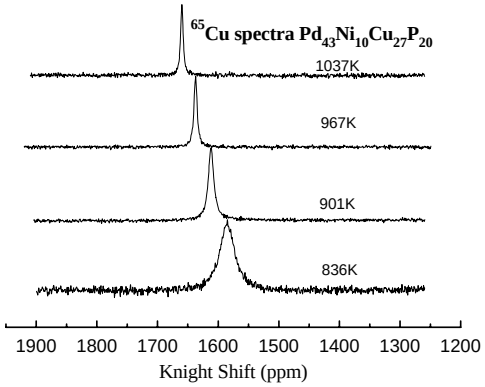

Figure 3. ^{65}Cu spectra in the supercooled liquid.

Figure 3 shows the ^{65}Cu NMR spectra in $Pd_{43}Ni_{10}Cu_{27}P_{20}$ near T_{liq}=870 K. It is quite clear that the sensitive range of ^{65}Cu linewidth falls at the right temperature range of our interest, namely, near and below T_{liq}. Both ^{63}Cu and ^{65}Cu NMR can be used for this study. The slight differences in the Larmor frequency and quadrupole moment between these two nuclei allow us to have an independent check of data interpretations. Figure 4 shows the measured temperature dependence of the linewidth over a wide temperature range. Over this temperature range, the Knight shift of both ^{31}P and ^{63}Cu and ^{65}Cu change linearly with temperature as shown in the inset of Fig. 4. In contrast, the correlation time τ_c increases dramatically upon decreasing temperature. Figure 5 plots the quantity $(\Delta\nu)^{-1/\gamma}$ ($\Delta\nu$ is the linewidth) versus temperature where $\gamma = 2.9$ is chosen. We see quite good linear temperature dependence below 900 K with an intercept at 700 K. This implies that

$$\tau_c^{-1/\gamma} \propto (\Delta\nu)^{-1/\gamma} \propto \left(\frac{T - T_c}{T_c}\right) \qquad (2)$$

with $T_c = 700$ K and $\gamma = 2.9$. This result is quite consistent with the prediction of the MCT, neutron scattering studies, and our previous result of rattling motion.

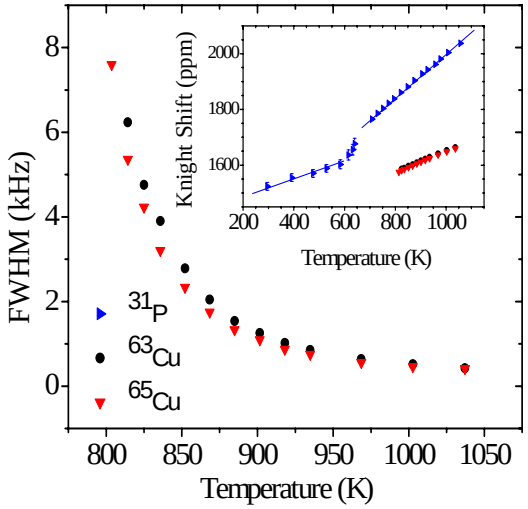

Figure 4. *T*-dependence of ^{65}Cu and ^{63}Cu linewidth. The *T*-dependence of the Knight shift is shown in the inset.

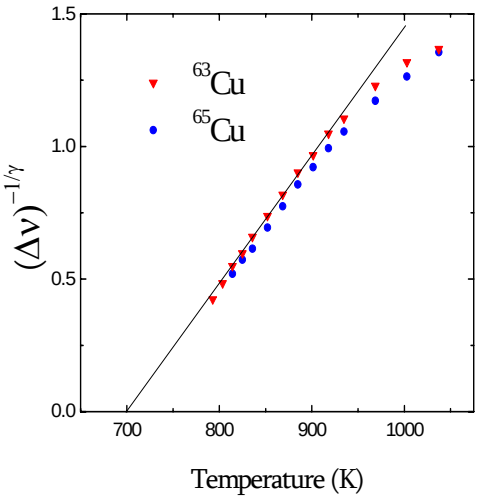

Figure 5. $(\Delta\nu)^{-1/\gamma}$ is plotted versus *T* where $\gamma = 2.9$ is chosen.

Based on these measurements and our previous data on the rate of P atomic motions, as determined from the motional narrowing of ^{31}P linewidth and stimulated echo techniques, we obtained a rather complete picture of atomic motions in PdNiCuP. This is shown in Figure 6. Comparing to results of previous diffusion measurements, it is clearly demonstrated that atomic motions of different elements in PdNiCuP are all very similar above T_c. Below T_c, motions of larger elements slow down much faster than the smaller element P. T_c is clearly the temperature below which atomic motions become more solid-like whereas above T_c it is liquid-like.

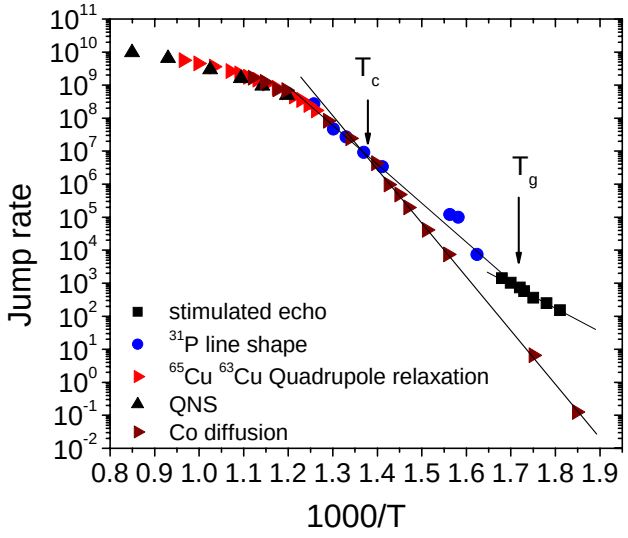

Figure 6. Atomic jump rate determined by various NMR methods. For comparison, the neutron and diffusion data are also shown.

2. Detection of quenched-in nuclei in $Al_{92}Sm_8$ metallic glasses

In addition to BMGs, we studied Al-based metallic glasses because of their potential applications as lightweight materials. We focused on the study of binary metallic glass $Al_{92}Sm_8$ in collaboration with Prof. Perepezko's group. Figure 7 shows the ^{27}Al NMR spectra of $Al_{92}Sm_8$ metallic glasses. Based on the XRD and TEM analysis, the two melt-spun $Al_{92}Sm_8$ samples are expected to be completely amorphous. The ^{27}Al spectra of the two glassy samples show that there is a sharp peak at 1600 ppm shift in both samples. This peak becomes much bigger upon annealing. Comparing this peak with that of the pure aluminum shows that the environment associated with this sharp feature is nearly identical to that of fcc Al environment. We have done detailed analysis of this environment through determination of the residual electric field gradient at such site. It becomes clear that quenched-in fcc-like Al nuclei exist in $Al_{92}Sm_8$ glassy samples. The amount of this depends sensitively on quenching conditions but so far none of the conditions are sufficient to eliminate such quenched-in nuclei. Less than 1 at% of Al in such quenched-in nuclei can be detected by NMR. This observation might be very relevant to the understanding of the glass forming ability of Al-based metallic glasses. Therefore, NMR will be a very valuable tool in developing Al-based metallic glasses that are important for the development of lightweight vehicles.

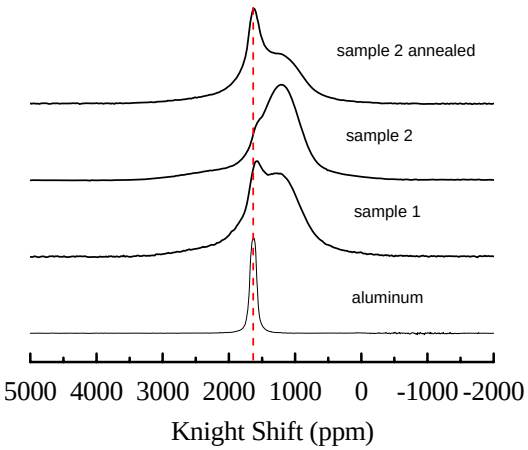

Figure 7. ^{27}Al spectra of $Al_{92}Sm_8$ metallic glass sample 1 (slower quenching rate), sample 2 (faster quenching rate), and sample 2 annealed at 130°C. The spectrum of pure aluminum is also shown.

3. Characterization of chemical bonding

Figure 8 shows ^{27}Al spectra of three types of BMGs. The Ce-based BMGs are discovered recently. It has a very low T_{liq} of 714 K and T_g of 359 K. Glassy rod samples of 3 mm in diameter can be produced with this material. The recently discovered $Y_{36}Sc_{20}Al_{24}Ni_{10}Co_{10}$ BMG has an extremely high GFA. Glassy rod samples of 2 cm in diameter can be produced with this material. The recently discovered Cu-Zr-Al system is also quite intriguing. BMGs can be produced with the corresponding binary system of Cu-Zr whereas addition of a small amount of Y can improve the GFA of the Cu-Zr-Al system dramatically. We noticed several intriguing features in the ^{27}Al spectra in Fig. 8. The shifts of the peaks are very unusual for all these BMGs especially for $Y_{36}Sc_{20}Al_{24}Ni_{10}Co_{10}$, $Cu_{45}Zr_{45}Al_{10}$, and $Cu_{47}Zr_{47}Al_6$. The shift is extremely small in all these three systems, especially in $Cu_{45}Zr_{45}Al_{10}$ and $Cu_{47}Zr_{47}Al_6$. What does this imply? In metallic systems the dominant shift mechanism is the Knight shift. The main contribution (especially for aluminum) K_s originates from the Fermi contact hyperfine interaction and can be expressed as

$$K_s = \frac{16\pi}{3}\,\mu_B^2 \left\langle |\psi(0)|^2 \right\rangle_{E_F} \Omega g(E_F) \qquad (3)$$

where $\left\langle |\psi(0)|^2 \right\rangle_{E_F}$ is the density of the electron wave function at the nucleus (only s-wave character is non-zero at the nucleus) averaged over all states at the Fermi level E_F and is normalized over an arbitrarily chosen volume Ω. $g(E_F)$ is the density of states per unit volume at the Fermi level. A small shift means that the density of states at the Fermi level has very small s character at the Al sites. This is unexpected for a metallic system. The shift in pure aluminum metal is around 1600 ppm. Subtracting the chemical shift contribution, which can be up to 200 ppm, the contribution of the Knight shift to the overall shift is less than 200 ppm in $Y_{36}Sc_{20}Al_{24}Ni_{10}Co_{10}$, $Cu_{45}Zr_{45}Al_{10}$, and $Cu_{47}Zr_{47}Al_6$. This indicates that the chemical bonding at the Al sites has strong covalent character. The Fermi contact hyperfine interaction also contributes to the nuclear spin-lattice relaxation rate $1/T_1$ given by

$$T_1^{-1} = \frac{64}{9}\pi^3 \hbar^3 \gamma_e^2 \gamma_n^2 \left\langle |\psi(0)|^2 \right\rangle_{E_F}^2 g^2(E_F) k_B T \qquad (4)$$

where γ_e and γ_n are the electron and nucleus gyromagnetic ratios. We measured $1/T_1$ and it is consistent with the conclusion that the density of states at the Fermi level is very low in $Y_{36}Sc_{20}Al_{24}Ni_{10}Co_{10}$, $Cu_{45}Zr_{45}Al_{10}$, and $Cu_{47}Zr_{47}Al_6$. Figure 9 shows the ^{65}Cu NMR spectra of $Ce_{70}Al_{10}Cu_{10}Ni_{10}$, $Ce_{70}Al_{10}Cu_{20}$, $Cu_{45}Zr_{45}Al_{10}$, and $Cu_{47}Zr_{47}Al_6$ BMGs. The Knight shifts of ^{65}Cu in $Cu_{45}Zr_{45}Al_{10}$ and $Cu_{47}Zr_{47}Al_6$ are 1300 and 1100 ppm, respectively, significantly smaller than that of pure copper at 2300 ppm. However, a shift of over 1000 ppm still represents a strong metallic character unlike that at the Al sites. We also noticed that increasing the Al content from 6 to 10 at% (not much effect below 6 at%) increases the ^{65}Cu Knight shift (thus the density of states at Cu sites) notably (Fig. 9) although the shift of ^{27}Al peak decreases very slightly at the same time (Fig. 8). This might explain the decrease of GFA when the Al content goes from 6 to 10 at%. This result suggests that a balance has to be observed in the process of optimizing the GFA. Adding Al to CuZr introduces covalent bonding which favors chemical short-range order and obviously improved the GFA over that of CuZr. However, too much Al could also lead to unfavorable effect, namely, increasing the density of states at the Fermi level at the Cu sites thus increasing the electronic energy.

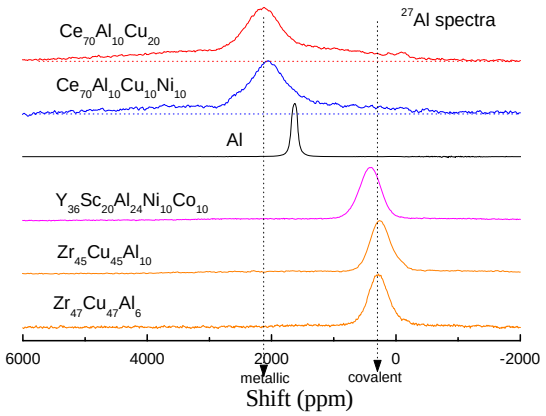

Figure 8. RT ^{27}Al spectra at 9.4 Tesla.

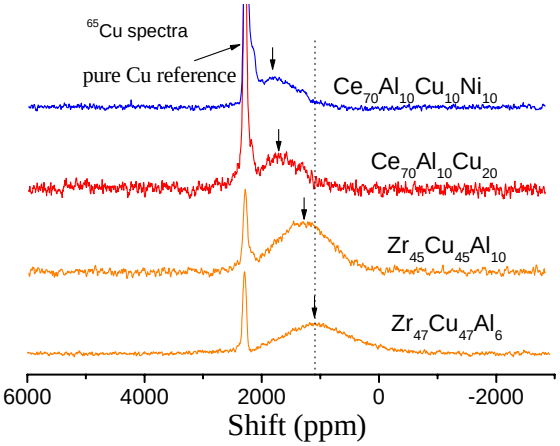

Figure 9. RT ^{65}Cu spectra at 9.4 T.

Our NMR results have revealed a wide range of properties of metallic glasses and supercooled liquids. We have also done systematic studies of fractures as described in detail in our Phys. Rev. Lett. paper. These studies have significantly increased our understanding of metallic glasses and glass transition at microscopic level. It should provide important information for the further development of bulk metallic glasses. It opens the door, for instance, for investigating the micro-alloying effect in many alloys where GFA was enhanced dramatically micro-alloying.